

# Correlation function of random heteropolymer solutions

Zh. S. Gevorkian<sup>1,2,\*</sup> and Chin-Kun Hu<sup>1,+</sup>

<sup>1</sup>*Institute of Physics, Academia Sinica, Nankang, Taipei 11529, Taiwan*

<sup>2</sup>*Institute of Radiophysics and Electronics*

*and Yerevan Physics Institute, Alikhanian Br.2*

*375036 Yerevan Armenia*

We study the density-density correlation function of the dense random heteropolymer solutions. We show that a phase transition is possible due to the heterogeneity of polymers. We also show that the critical behavior of the system is described by the  $O(N)$  model at  $N = 0$ .

PACS number(s): 61.25.Hq

## I. INTRODUCTION

Random heteropolymers are of great interests because of their wide occurrence in nature, e.g. many biopolymers are random heteropolymers. It is well known that they have many unusual properties [1–3]. For example, when the temperature decreases they experience microphase separation and freezing phase transitions. The protein folding is also an example of such a property. However all of these properties refer mainly to a single heteropolymer. The properties of polymer solutions have been well studied [4,5]. One of the well known properties is the screening of excluded volume interactions in polymer solutions. It leads to an exponential decrease of the density-density correlation function with distance. In two dimensions, some peculiarities appear in the behavior of the correlation function. It turns out that the excluded volume effects lead to a phase transition in a dense polymer solution [6]. The ordered phase is described by the low temperature phase of  $N = 0$  vector model [7]. One of the features of the ordered phase is that the correlation function increases with distance.

Along with the single heteropolymers and polymer solutions, it is interesting to investigate also heteropolymer solutions. In this paper this problem is investigated for the first time. We will see below that a phase transition is possible due to the heterogeneity of polymer chains.

The paper is organized as follows. In Section II we derive an equation for the correlation function of a random heteropolymer solution. In Section III we develop a diagram technique to treat with the heterogeneity random field. A critical heterogeneity parameter is introduced in Section IV. In Section V we show that the crossed diagrams for self-energy are smaller than the non-crossed ones. Then we sum the non-crossed diagrams and improve the mean field approximation. In Section VI we present a field-theoretical approach and show that the problem is reduced to the  $O(N)$  model at  $N = 0$ . Section VII concludes our results. In the Appendix, we justify the approximations done in Section II.

## II. INITIAL RELATIONS

The correlation function of a polymer solution is determined as follows

$$G(\vec{r}) = \frac{1}{c} [ \langle c(\vec{r})c(0) \rangle - c^2 ], \quad (1)$$

where

$$c(\vec{r}) = \sum_i \delta(\vec{r} - \vec{R}_i), \quad (2)$$

is the microscopic concentration of monomers,  $\vec{R}_i$  is the coordinate of the  $i - th$  monomer,  $\langle \dots \rangle$  means the thermodynamic averaging and  $c$  is an average concentration of monomers. Note that Eq.(2) implies a summation over all chains and monomers. Now let us derive an equation for the correlation function (1). It can be represented in the form [4]

$$cG(\vec{r}) = A \int \prod d\vec{R}_i c(\vec{r})c(0) \exp \left[ -\frac{U}{T} \right], \quad (3)$$

where  $U$  is the conformational energy of polymers and  $A$  is a normalization constant

$$A = \int \prod d\vec{R}_i \exp \left[ -\frac{U}{T} \right]. \quad (4)$$

The conformational energy consists of elastic and excluded volume parts

$$\frac{U}{T} = \frac{\alpha}{2a^2} \sum_{bn} (\vec{R}_{bn} - \vec{R}_{bn-1})^2 + \frac{1}{2} \sum_{ij} v_{ij} \delta(\vec{R}_i - \vec{R}_j). \quad (5)$$

Here  $\alpha = 3, 2$  for three and two dimensions, respectively, the index  $b$  denotes a polymer chain and  $n$  is the number of a monomer in a chain,  $a$  is the average size of monomers,  $i \equiv b, n$  and  $v_{ij}$  are the random excluded volume constants. It is convenient in (3) to go to integration on the monomer concentration  $c(\vec{r})$  instead of  $R_i$ . For this purpose one has to express the conformational energy  $U$  in terms of monomer concentration. It is well known [4] that the elastic energy of a polymer solution, in the Gaussian approximation, can be represented in the form

$$\frac{U_{el}}{T} = \frac{BV}{2} \sum_{\vec{k}} a^2 k^2 c_{\vec{k}} c_{-\vec{k}} \quad (6)$$

where  $B = 1/12c, 1/8c$  for three [4] and two dimensions, respectively,  $V$  is the volume of the system and  $c_{\vec{k}}$  is the Fourier transform of  $c(\vec{r})$

$$c_{\vec{k}} = \frac{1}{V} \int c(\vec{r}) e^{i\vec{k}\vec{r}} d\vec{r}. \quad (7)$$

Note that the approximation (6) is justified in the concentrated solutions where the density fluctuations are small [4]. It is convenient to represent the random excluded volume constant in the form  $v_{ij} = v + \delta v_{ij}$ , where  $v$  is the average excluded volume constant and  $\delta v_{ij}$  is the fluctuating part with the average  $\langle \delta v_{ij} \rangle = 0$ . Using Eqs.(2) and (5) for the average part of excluded volume energy, one finds

$$\frac{U_{exc}^{av}}{T} = \frac{v}{2} \int d\vec{r} c^2(\vec{r}). \quad (8)$$

It is shown in the Appendix that if  $\delta v_{ij}$  are independent random variables with the variance  $\langle \delta v_{ij}^2 \rangle = w^2$  [8] then the fluctuating part of excluded volume energy can be represented in the form

$$\frac{U_{exc}^1}{T} = \frac{1}{2} \int v_1(\vec{r}) c^2(\vec{r}) d\vec{r}, \quad (9)$$

where  $v_1(\vec{r})$  is a Gaussian distributed random function with  $\delta$  correlations

$$\langle v_1(\vec{r}) v_1(\vec{r}') \rangle = \frac{w^2}{c} \delta(\vec{r} - \vec{r}'), \quad \langle v_1 \rangle = 0. \quad (10)$$

Using Eqs.(6), (8) and (9) for the conformational energy of a random heteropolymer solution, finally we obtain

$$\frac{U}{T} = \frac{U_{el} + U_{exc}^{av} + U_{exc}^1}{T} = \frac{1}{2} \int d\vec{r} c(\vec{r}) \left[ -Ba^2 \nabla^2 + v + v_1(\vec{r}) \right] c(\vec{r}). \quad (11)$$

Now the correlation function (1) can be written in terms of a functional integral over  $c(\vec{r})$  [4]

$$cG(\vec{r}) = A \int Dc(\vec{r}) c(\vec{r}) c(0) \exp \left[ -\frac{U[c(\vec{r})]}{T} \right], \quad (12)$$

where

$$Dc(\vec{r}) = \prod_{k>0} dc_{\vec{k}}. \quad (13)$$

The symbol  $\prod_{k>0}$  means an integration over the independent components  $c_{\vec{k}}$ . Because the relation  $c_{\vec{k}}^* = c_{-\vec{k}}$  (this follows from the fact that  $c(\vec{r})$  is a real function) not all the components of  $c_{\vec{k}}$  are independent. Calculating the Gaussian integral over  $c(\vec{r})$  in Eq.(12), one finds

$$cG(\vec{r}) = \left[ -Ba^2 \nabla^2 + v + v_1(\vec{r}) \right]^{-1} \delta(\vec{r}). \quad (14)$$

It is easy to obtain the equation for  $G(\vec{r})$  from Eq.(14)

$$\left[ \nabla^2 - \xi^{-2} - \xi^{-2} \frac{v_1(\vec{r})}{v} \right] G(\vec{r}) = -\frac{\xi^{-2}}{vc} \delta(\vec{r}). \quad (15)$$

Here  $\xi = (Ba^2/v)^{1/2}$  is the correlation length of the polymer solution.

### III. IMPURITY DIAGRAM TECHNIQUE

For bare correlation function with  $v_1 = 0$ , which corresponds to homopolymer solution, one has from (15)

$$G_0(q) = \frac{\xi^{-2}}{vc(q^2 + \xi^{-2})}. \quad (16)$$

In the coordinate representation we have from Eq.(16)

$$G_0(\vec{r}) = \frac{\xi^{-2}}{vc} \int \frac{d\vec{q}}{(2\pi)^d} \frac{\exp(i\vec{q}\vec{r})}{q^2 + \xi^{-2}}. \quad (17)$$

Using the method of steepest descent in the integral of Eq. (17) over the momentum [9], we can find the asymptotic behavior of correlation function on large distances

$$G_0(\vec{r}) \sim \frac{\xi^{-1}}{2vc} \left( \frac{\xi^{-1}}{2\pi r} \right)^{\frac{d-1}{2}} e^{-\frac{r}{\xi}}. \quad (18)$$

It follows from Eq.(18) that the correlation function at large distances decreases exponentially with the correlation length  $\xi$ .

Now we construct a perturbation theory with the heterogeneity parameter  $v_1$ . It is convenient to deal with the dimensionless in  $d = 2$  correlation function  $G(\vec{r}) \equiv G(\vec{r})vc\xi^2$  that satisfies the equation

$$\left[ \nabla^2 - \xi^{-2} - \xi^{-2} \frac{v_1(\vec{r})}{v} \right] G(\vec{r}) = -\delta(\vec{r}). \quad (19)$$

In order to construct a perturbation theory in the heterogeneity parameter, we use the impurity diagram technique [10]. It is easy to obtain the following expansion from Eq.(19)

$$\mathbf{G} = \text{——} = \text{——} + \text{——} \Sigma \text{——} + \text{——} \Sigma \text{——} \Sigma \text{——} + \dots, \quad (20)$$

where the self-energy  $\Sigma$  is determined by the following irreducible diagrams

$$\Sigma = \text{——} + \text{——} + \text{——} + \dots. \quad (21)$$

The heavy line in Eq.(20) denotes the averaged correlation function, the thin one denotes the bare correlation function of Eq. (16) and the dashed one is the Fourier transform of the heterogeneity random field correlation function of Eq.(15),  $\xi^{-4}w^2/(cv^2)$ . Summing the diagrams in Eq.(20), we have the following Dyson equation

$$\text{——} = \text{——} + \text{——} \Sigma \text{——}. \quad (22)$$

It has a solution

$$G(q) = \frac{1}{q^2 + \xi^{-2} - \Sigma(q)}, \quad (23)$$

where the self-energy is determined by diagrams of Eq. (21). In the leading order, we get for the self-energy

$$\begin{aligned}\Sigma_0(q) &= \frac{\xi^{-4}w^2}{cv^2} \int \frac{d\vec{k}}{(2\pi)^d} G_0(\vec{q} - \vec{k}) = \frac{\xi^{-4}w^2}{4\pi cv^2} \ln(1 + \frac{\xi^2}{v}) \quad \text{for } d = 2, \text{ and} \\ &= \frac{\xi^{-4}w^2}{2\pi^2 cv^2} \left( \frac{1}{v^{1/3}} - \frac{\pi}{2\xi} \right) \quad \text{for } d = 3.\end{aligned}\quad (24)$$

The divergence of the integral in the upper limit in Eq.(24) is caused by the  $\delta$  feature of the excluded volume interaction of Eq.(5). It is obvious that it should be smoothed on the scales less than  $v^{1/d}$ . Therefore we cut the upper limit of the integral in Eq.(24) by this value.

It follows from Eqs.(23) and (24), that the “mass” term in the denominator of correlation function of Eq. (23) is renormalized as

$$\xi_R^{-2} = \xi^{-2} - \Sigma. \quad (25)$$

It follows from Eqs.(23)-(25), that the second term in Eq.( 25) at some critical value of heterogeneity parameter  $w^2/v^2$  can become equal to the first one. In this case the correlation length diverges and the exponential decay of the correlation function of Eq. (18) at large distances will be substituted by a power law. This is a second order phase transition caused by the heterogeneity of polymers.

#### IV. CRITICAL HETEROGENEITY PARAMETER

It is easy to obtain the critical value of the heterogeneity parameter  $g = w^2/v^2$  from the condition of divergence of the renormalized correlation length. Using Eqs. (24)-(25), one has

$$\begin{aligned}g_c &= \frac{4\pi c \xi^2}{\ln(1 + \xi^2/v)} \quad \text{for } d = 2, \text{ and} \\ &= \frac{2\pi^2 c \xi^2}{1/v^{1/3} - \pi/2\xi} \quad \text{for } d = 3.\end{aligned}\quad (26)$$

Taking into account that almost always  $\xi \gg v^{1/3}$ , we can simplify the expression of Eq. (26) by

$$\begin{aligned}
g_c &= \frac{\pi a^2}{4v \ln \frac{a^2}{v\sqrt{8}\Phi}} \quad \text{for } d = 2, \text{ and} \\
&= \frac{\pi^2}{6} \left(\frac{a}{v^{1/3}}\right)^2 \quad \text{for } d = 3.
\end{aligned} \tag{27}$$

where  $\Phi = ca^2$  is the fraction of monomers in the solution. It follows from Eq.(27) that  $g_c$  does not depend on monomer concentration (only logarithmically in two dimensions). It is mainly determined by the stiffness parameter  $v/a^3$  ( $v/a^2$  in two dimensions) of polymer chains. It is also obvious from Eqs.(26)-(27) that the phase transition in heterogeneity parameter is more appropriately realized in a system of flexible chains  $v/a^3 \leq 1$  rather than in stiff  $v/a^3 \ll 1$  chains solution because the limit  $g \rightarrow g_c$  is easier reached in the first case. One can obtain from Eqs.(23)-(25) that near the critical point the renormalized correlation length diverges as

$$\xi_R \sim \xi \left(\frac{g_c - g}{g_c}\right)^{-1/2} \tag{28}$$

So, for the critical exponent of the correlation length in the phase  $g < g_c$  we obtain the mean field result. This means that tree approximation that we used in Eqs. (20), (23) and (24) for correlation function corresponds to the mean field theory. At the critical point  $g = g_c$  one has power law behavior for correlation function on large distances instead of the exponential decreasing in  $g < g_c$  case. In the next section we try to go beyond the mean field approximation.

## V. BEYOND THE MEAN FIELD APPROXIMATION

Let us consider the second order diagrams in the diagrammatic expansion of the self-energy in Eq.(21). For the contribution of the second diagram in (21), one has

$$\Sigma_2(q) = \left(\frac{\xi^{-4}w^2}{cv^2}\right)^2 \int \frac{d\vec{k}_1 d\vec{k}_2}{(2\pi)^{2d}} G^2(\vec{k}_1 - \vec{q}) G(\vec{k}_2 + \vec{k}_1 - \vec{q}). \tag{29}$$

We take the correlation functions in (29) in the tree approximation

$$G(k) = \frac{1}{k^2 + \xi_R^2} \tag{30}$$

where the renormalized correlation length is determined by Eq.(25) and  $\xi_R \rightarrow \infty$  at the critical point  $g = g_c$ . Substituting Eq. (30) into Eq. (29) and integrating over the momentums, we have

$$\begin{aligned}\Sigma_2 &= \left(\frac{\xi^{-4}w^2}{cv^2}\right)^2 \frac{\xi_R^2}{16\pi^2} \ln \frac{\xi_R^2}{v} \quad \text{for } d = 2, \text{ and} \\ &= \left(\frac{\xi^{-4}w^2}{cv^2}\right)^2 \frac{\xi_R}{8\pi^3 v^{1/3}} \quad \text{for } d = 3.\end{aligned}\quad (31)$$

When obtaining Eq.(31) we cut the upper limit of momentum integrals in Eq.(30) at  $1/v^{1/d}$  and believe that  $\xi_R \gg v^{1/d}$  which is always correct in the critical region  $g \rightarrow g_c$ . Now consider the contribution of the third diagram in Eq.(21). It can be represented in the form

$$\Sigma_3(q) = \left(\frac{\xi^{-4}w^2}{cv^2}\right)^2 \int \frac{d\vec{k}_1 d\vec{k}_2}{(2\pi)^{2d}} G(k_1) G(\vec{k}_1 + \vec{k}_2) G(\vec{k}_2 - \vec{q}). \quad (32)$$

Substituting Eq.(30) into Eq.(31) and going to the dimensionless variables of integration, one has

$$\Sigma_3(q) = \left(\frac{\xi^{-4}w^2}{cv^2}\right)^2 \xi_R^{2d-6} \int \frac{d\vec{k}_1 d\vec{k}_2}{(2\pi)^{2d}} \frac{1}{(k_1^2 + 1)(k_2^2 + 1)} \frac{1}{(\vec{k}_1 + \vec{k}_2 + \vec{q})^2 + 1}. \quad (33)$$

We are mainly interested in the large distance behavior of the correlation function. Our analysis of the integral in Eq.(33) at the limit  $q \rightarrow 0$  shows that

$$\begin{aligned}\Sigma_3(0) &\sim \left(\frac{\xi^{-4}w^2}{cv^2}\right)^2 \frac{\xi_R^2}{16\pi^2} \quad \text{for } d = 2, \text{ and} \\ &\sim \left(\frac{\xi^{-4}w^2}{cv^2}\right)^2 \frac{1}{8\pi^3} \ln \frac{\xi_R}{v^{1/3}} \quad \text{for } d = 3.\end{aligned}\quad (34)$$

Comparing Eq.(34)with the Eq.(31) one can see that in the critical region  $\xi_R \gg v^{1/d}$  the crossed diagrams ,because the additional integration over angles, (see also [10]) have an additional smallness on parameter  $v^{1/d}/\xi_R \ll 1$ . So, in the critical region the non-crossed diagrams are the dominant ones and we can sum them

$$\Sigma = \text{Diagram} + \text{Diagram} + \text{Diagram} + \dots \quad (35)$$

The sum of the diagrams can be represented in the form

$$\begin{aligned}\Sigma_R &= \frac{\Sigma_0}{1 - \frac{\xi^{-4}w^2}{cv^2} \int \frac{d\vec{k}}{(2\pi)^d} G^2(k)} = \frac{\Sigma_0}{1 - \frac{\xi^{-4}w^2}{cv^2} \frac{\xi_R^2}{4\pi}} \quad \text{for } d = 2, \text{ and} \\ &= \frac{\Sigma_0}{1 - \frac{\xi^{-4}w^2}{cv^2} \frac{\xi_R}{4\pi}} \quad \text{for } d = 3.\end{aligned}\quad (36)$$

The expressions are correct provided that  $\xi^{-4}w^2\xi_R/4\pi cv^2 < 1$ . At the critical point  $\xi_R \rightarrow \infty$ . Therefore, even this improved approximation which corresponds the one-loop correction in field theoretical calculation still breaks down. To investigate the critical region  $g \rightarrow g_c$  more carefully and to describe the ordered phase  $g > g_c$ , we use a field theoretical approach in the next section.

## VI. FIELD THEORETICAL APPROACH

It follows from Eqs.(19)-(25) and (27) that the renormalized correlation function satisfies the equation

$$[-\nabla^2 + m^2 + h(\vec{r})] G(\vec{r}) = \delta(\vec{r}), \quad (37)$$

where  $m^2 = \xi^{-2}(g_c - g)/g_c$  is the renormalized “mass” term and  $h(\vec{r}) = \xi^{-2}v_1(\vec{r})/v$  is the heterogeneity random field. To carry out the averaging over the realizations of random field, we use a functional integral to represent the correlation function:

$$G(\vec{r}) = \frac{-i \int D\varphi(\vec{r}) \varphi(\vec{r}) \varphi(0) \exp S_0}{\int D\varphi(\vec{r}) \exp S_0}, \quad (38)$$

where

$$S_0 = -\frac{i}{2} \int d\vec{r} \varphi(\vec{r}) [-\nabla^2 + m^2 + h(\vec{r})] \varphi(\vec{r}). \quad (39)$$

Here  $\varphi(\vec{r})$  is a real field. Introducing the replica fields and using Eq. (39), one can represent the correlation function in the form

$$G(\vec{r}) = \frac{-i \int \prod D\varphi_\alpha(\vec{r}) \varphi_1(\vec{r}) \varphi_1(0) \exp S_N}{\int \prod D\varphi_\alpha(\vec{r}) \exp S_N}, \quad (40)$$

where

$$S_N = -\frac{i}{2} \int d\vec{r} \varphi_\alpha(\vec{r}) \left[ -\nabla^2 + m^2 + h(\vec{r}) \right] \varphi_\alpha(\vec{r}). \quad (41)$$

In Eq.(41), a summation over the repeated indexes is implied. Carrying out a Gaussian integration over  $\varphi_\alpha$  in denominator of Eq.(40), one has

$$\int \prod D\varphi_\alpha(\vec{r}) \exp S_N = \left( \det \left[ \frac{-\nabla^2 + m^2 + h(\vec{r})}{-2\pi i} \right] \right)^{-N/2}. \quad (42)$$

Finally, taking into account Eqs.(40) and (42) we obtain the following representation for the correlation function

$$G(\vec{r}) = \lim_{N \rightarrow 0} -i \int \prod D\varphi_\alpha(\vec{r}) \varphi_1(\vec{r}) \varphi_1(0) \exp S_N. \quad (43)$$

Now using Eq.(43), one can carry out the Gaussian averaging over the random field  $h(\vec{r})$

$$G(\vec{r}) = \lim_{N \rightarrow 0} -i \int \prod D\varphi_\alpha(\vec{r}) \varphi_1(\vec{r}) \varphi_1(0) \exp S, \quad (44)$$

where

$$S = -\frac{i}{2} \int d\vec{r} \varphi_\alpha(\vec{r}) \left[ -\nabla^2 + m^2 \right] \varphi_\alpha(\vec{r}) - \frac{H}{8} \int d\vec{r} \left[ \varphi_\alpha^2(\vec{r}) \right]^2. \quad (45)$$

Here  $H = \xi^{-4} w^2 / (cv^2)$ . So, we obtain a non-trivial field-theoretical model. Expanding  $\exp S$  in heterogeneity parameter  $H$  one can reproduce the impurity diagrams in Eq. (21).

So we map the concentrated random heteropolymer solution problem onto the  $O(N)$  vector model at  $N = 0$ . This model is well studied [9] and we can use it's results. Remind that the problem of self-avoiding walk of a single polymer chain is also mapped to this model [11]. However there is an important difference between these two problems. In our case the ordered phase  $g > g_c$  (see below) also exists in contrary the former one where the criticality is reached in the limit of long chains  $L \rightarrow \infty$ .

Thus, we have the following behavior for the correlation function in the phase  $g < g_c$ . When  $g \ll g_c$  correlation function at large distances exponentially decreases with some correlation length. At  $g \rightarrow g_c$  correlation length diverges  $\xi \sim (g_c - g)^{-\nu}$ . The value of

the exponent  $\nu$  is well known from the  $\epsilon - expansion$  and from the numerical calculations  $\nu \approx 3/5, 3/4$ , for three and two dimensions, respectively. At the critical point the correlation function has a power law behavior  $G(r) \sim 1/r^{d-2+\eta}$ . The exponent  $\eta$  is also well known for  $O(N)$  model. This power law behavior is preserved also in the ordered phase in three dimensions. In two dimensions there are some peculiarities in the ordered phase. It follows from the preceding consideration that the phase transition is caused by the “massless” fluctuations. In the vicinity of the critical point we can simplify the action of Eq.(45) by separating the “massless” fluctuations. For this reason we find saddle-point trajectories of the action of Eq. (45). Differentiating (45), we obtain

$$i\nabla^2\varphi_\beta(\vec{r}) - im^2\varphi_\beta(\vec{r}) - \frac{H}{2}\varphi_\beta(\vec{r}) \sum_\gamma \varphi_\gamma^2(\vec{r}) = 0. \quad (46)$$

We are looking for the homogeneous solution of Eq. (46),  $\varphi_\beta(\vec{r}) = const$

$$-im^2\varphi_\beta - \frac{H}{2}\varphi_\beta \sum_\gamma \varphi_\gamma^2 = 0. \quad (47)$$

This equation has two solutions

$$\varphi_\beta = 0, \quad \sum_\gamma \varphi_\gamma^2 = -\frac{2im^2}{H}, \quad \beta, \gamma = 1, \dots, N. \quad (48)$$

It can be seen from Eq.(48) that the second type of saddle points lies in the complex plane. In the stationary phase method it is well known that in such cases one must transform the integration contour so that it passes through the saddle points (Fig. 1). We have in mind that the integration contour is transformed locally at each point  $\vec{r}$ . Along the new contour  $\varphi$  has the form  $\varphi = \varphi^R(1-i)$ , where  $\varphi^R$  is real. Suppose that the fluctuating fields locally satisfy the extremum condition of Eq. (48). Making a change of variables  $\varphi_\alpha(\vec{r}) = \sqrt{m^2/H}\varphi_\alpha^R(1-i)$ , we obtain the following expression for the effective action describing the “massless” fluctuations

$$S_{eff} = -\frac{m^2}{H} \int d\vec{r} (\vec{\nabla} \varphi_\alpha)^2, \quad (49)$$

where

$$\sum_\alpha \varphi_\alpha^2(\vec{r}) = 1. \quad (50)$$

Here, for brevity, we omit the index  $R$  and neglect the constant terms in action that do not affect the critical behavior. So, the critical behavior of random heteropolymer solution is described by the non-linear  $\sigma$  model at  $N = 0$ . The coupling constant of the model of Eq. (49) is  $m^2/H = c\xi^2(g_c - g)/(gg_c)$ . The region  $g < g_c$  corresponds to the high temperature phase of  $N = 0$  vector model [12]. Note that our derivation of  $\sigma$  model from the  $(\varphi^2)^2$  model is correct in the high temperature phase  $g < g_c$ . It is well known [9] that at the critical point the correlation functions of the non-linear  $\sigma$ -model and  $(\varphi^2)^2$  theory are identical. However  $(\varphi^2)^2$  model is renormalizable at  $d \leq 4$  but  $\sigma$  model is renormalizable only at  $d \leq 2$ . So, in the critical domain for  $d = 2$  one can use the non-linear  $\sigma$ -model instead of the  $(\varphi^2)^2$ -model. The ordered phase  $g > g_c$  will be described by the low-temperature phase of the non-linear  $\sigma$ -model at  $N = 0$ . However the coupling constant in this case differs from that of Eq.(50). It will be proportional to the expectation value of the order parameter which is non-zero in the ordered phase [9]. Note that this transition to the low-temperature phase of  $N = 0$  vector model in two-dimension is caused by the heterogeneity of chains and not by dense polymer self-avoiding walks [6]. The low-temperature phase of  $N = 0$  vector model has many unusual properties. One of them is the increasing of spin-spin correlation function with distance [7]. In our case this means that in the phase  $g > g_c$  the correlation function will increase with distance. The corresponding power index is  $3/8$  [7] . In the dense polymer case such a behavior is explained by the repelling of the extremities of chains. To understand this result for the heteropolymer solution, consider the case when each chain consists of only two kinds of monomers (see Appendix). In this case there will be three excluded volume constants  $v_{aa}$ ,  $v_{ab}$  and  $v_{bb}$ . Suppose that the excluded volume constants between monomers largely differ from each other so that  $v_{ab}$ ,  $v_{bb} \gg v_{aa}$  (see also Appendix). In order to minimize the conformational energy, type  $a$  monomer prefers contact with type  $a$  monomers. This means that the compensation of excluded volume interactions leading to the screening effect in polymer solutions will be violated in random heteropolymer solution. Moreover, the strong repulsion between different kinds of monomers will lead to the microphase separation like the analogous effect in single random heteropolymers (see

[1] and [2] and references therein). Although these papers mainly dealt with the compact conformations of single random heteropolymers (which is the case  $v < 0$ , in our case always  $v > 0$ ), nevertheless we think that these two phenomena are closely related. The microphase separation is the main reason of the rise of anti-correlations in heteropolymer solutions in two dimensions and power law decreasing of correlation function in three dimensions.

## VII. CONCLUSION

We have considered the effect of random heterogeneity on the density-density correlation function of dense polymer solutions. It turns out that a phase transition is possible due to the heterogeneity of the polymer chains. The heterogeneity parameter is determined by the ratio of variance and average values of excluded volume constant. The critical behavior is described by the  $O(N)$  vector model at  $N = 0$ . The anti- correlation behavior of correlation function in two dimensions and the power law behavior in three dimensions in the ordered phase are associated with the microphase separation.

This work was supported in part by the National Science Council of the Republic of China (Taiwan) under the grant no. NSC 89-2112-M001-005.

## Appendix: Random Excluded Volume Constant

Using (2), one can represent the fluctuating part of excluded volume energy in the form

$$\frac{U_{exc}^1}{T} = \frac{1}{2} \int d\vec{r} \sum_{ij} \delta v_{ij} \delta(\vec{r} - \vec{R}_i) \delta(\vec{r} - \vec{R}_j). \quad (51)$$

Suppose that  $\delta v_{ij}$  are independent random variables with variance  $w$ . Then for the large number of monomers because of the central limit theorem, one has

$$\sum_j \delta v_{ij} \delta(\vec{r} - \vec{R}_j) \equiv v_i(\vec{r}) c(\vec{r}). \quad (52)$$

where  $v_i$  are random Gaussian variables with zero average and variance  $w$ . To prove Eq. (52), we calculate the averages and variances of left and right hand sides of Eq. (52). It is

evident that  $\langle v_i \rangle = 0$  because  $\langle \delta v_{ij} \rangle = 0$ . Now calculate the variance of the left hand side of Eq. (52),

$$\sum_{jk} \langle \delta v_{ij} \delta(\vec{r} - \vec{R}_j) \delta v_{ik} \delta(\vec{r} - \vec{R}_k) \rangle = \sum_{jk} \langle \delta v_{ij} \delta v_{ik} \rangle \delta(\vec{r} - \vec{R}_i) \delta(\vec{r} - \vec{R}_k). \quad (53)$$

Because  $\delta v_{ij}$  are independent random variables, one has

$$\langle \delta v_{ij} \delta v_{ik} \rangle = \delta_{jk} w^2. \quad (54)$$

Substituting Eq.(54) into Eq.(53), we have

$$\sum_{jk} \langle \delta v_{ij} \delta v_{ik} \rangle \delta(\vec{r} - \vec{R}_j) \delta(\vec{r} - \vec{R}_k) = w^2 c^2(\vec{r}). \quad (55)$$

It is evident that the variance of right hand side of (52) is also  $w^2 c^2(\vec{r})$ . Substituting Eq.(52) into Eq.(51) for the fluctuating part of excluded volume energy, we have

$$\frac{U_{exc}^1}{T} = \frac{1}{2} \int d\vec{r} c(\vec{r}) \sum_i v_i(\vec{R}_i) \delta(\vec{r} - \vec{R}_i). \quad (56)$$

Let us prove that

$$\sum_i v_i \delta(\vec{r} - \vec{R}_i) \equiv v_1(\vec{r}) c(\vec{r}), \quad (57)$$

where  $v_1(\vec{r})$  is a Gaussian distributed random function with  $\delta$ -correlations. It is evident that  $\langle \sum_i v_i \delta(\vec{r} - \vec{R}_i) \rangle = 0$ . Now let us calculate the correlator

$$K(\vec{r}, \vec{r}') = \sum_{ij} \langle v_i v_j \rangle \delta(\vec{r} - \vec{R}_j) \delta(\vec{r}' - \vec{R}_j). \quad (58)$$

The  $v_i$  are independent Gaussian variables, therefore  $\langle v_i v_j \rangle = \delta_{ij} w^2$ . Substituting this into the Eq.(58), we have

$$K(\vec{r}, \vec{r}') = w^2 \sum_{ij} \delta_{ij} \delta(\vec{r} - \vec{R}_i) \delta(\vec{r}' - \vec{R}_j). \quad (59)$$

For the dense solution of heteropolymers one can go to the continuous limit  $\delta_{ij} \rightarrow \delta(\vec{R}_i - \vec{R}_j)/c$ ,

$$K(\vec{r}, \vec{r}') = \frac{w^2}{c} \sum_{ij} \delta(\vec{R}_i - \vec{R}_j) \delta(\vec{r} - \vec{R}_i) \delta(\vec{r}' - \vec{R}_j). \quad (60)$$

Using the properties of  $\delta$  functions, one has

$$K(\vec{r}, \vec{r}') = \frac{w^2}{c} \delta(\vec{r} - \vec{r}') c(\vec{r}) c(\vec{r}'). \quad (61)$$

So the function  $\sum v_i \delta(\vec{r} - \vec{R}_i)$  is equivalent to the function  $v_1(\vec{r}) c(\vec{r})$ . Finally, for the random part of excluded volume energy, we have

$$\frac{U_{exc}^1}{T} = \frac{1}{2} \int d\vec{r} v_1(\vec{r}) c^2(\vec{r}) \quad (62)$$

which coincides with Eq. (9).

Now consider a special case when each chain contains only two types of monomers. Suppose that each heteropolymer consists of  $a$  and  $b$  type monomers with  $1 - f$  and  $f$  fractions, respectively. Consider the case when  $f \ll 1$  and  $v_a \ll v_b$ . Here  $v_a \equiv v_{aa}$  and  $v_b \equiv v_{ab}$ . As the effect of  $v_{bb}$  will be proportional to  $f^2 \ll 1$ , we can ignore it. In such conditions the average excluded volume constant can be estimated as

$$v = (1 - f)v_a + fv_b. \quad (63)$$

The variance (dispersity) of the excluded volume constant is estimated as

$$w^2 = f(1 - f)(v_b - v_a)^2. \quad (64)$$

The heterogeneity parameter for this type of randomness will be

$$g = \frac{w^2}{v^2} = \frac{f(1 - f)(v_b - v_a)^2}{[(1 - f)v_a + fv_b]^2}. \quad (65)$$

Assume that  $fv_b \ll (1 - f)v_a$  then we get from Eqs. (63) and (65)

$$v \approx v_a, \quad g \sim f \frac{v_b^2}{v_a^2}. \quad (66)$$

Although  $fv_b/v_a \ll 1$ , the heterogeneity parameter can be large

$$g \sim \frac{fv_b}{v_a} \frac{v_b}{v_a}. \quad (67)$$

because of  $v_b \gg v_a$ . As can be seen from Eq.(66), in this particular case the average excluded volume constant is determined mainly by type  $a$  monomers and the dispersity is determined by type  $b$  monomers.

## REFERENCES

\* Electronic address: gevork@uniphi.yerphi.am

† Electronic address: huck@phys.sinica.edu.tw.

- [1] C. D. Sfatos and E. I. Shakhnovich, Phys. Reports **288**, 77 (1997).
- [2] A. Yu. Grosberg, Physics-Uspekhi **40**(2), 125 (1997).
- [3] E.G.Timoshenko,Yu.A.Kuznetsov,K.A.Dawson,Phys.Rev.E,**57**,6801 (1998).
- [4] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, New York, 1986).
- [5] P.G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).
- [6] B. Duplantier and H. Saleur, Nucl. Phys. B, **290** [FS20], 291 (1987).
- [7] B. Nienhuis, J. Stat. Phys. **34**, 731 (1984) and in *Phase Transitions and Critical Phenomena* vol. 11, eds.C. Domb and J.L.Lebowitz (Academic Press, London 1987).
- [8] J.-R. Roan and E.I. Shakhnovich, Phys. Rev. E **54**, 5340 (1996).
- [9] J.Zinn-Justin,Quantum Field Theory and Critical Phenomena, Clarendon Press,Oxford,(1996).
- [10] A.A. Abrikosov, L.P. Gor'kov, and I.E. Dzyaloshinskii, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hill, Englewood Cliffs, 1969).
- [11] P.G. de Gennes,Phys.Lett.A **38**,339,(1972).
- [12] H. Saleur, Phys. Rev. B **35**, 3657 (1987).

### Figure Caption

Fig. 1. Transformation of the integration contour in the complex  $\varphi$  plane.

## FIGURES

FIG. 1.

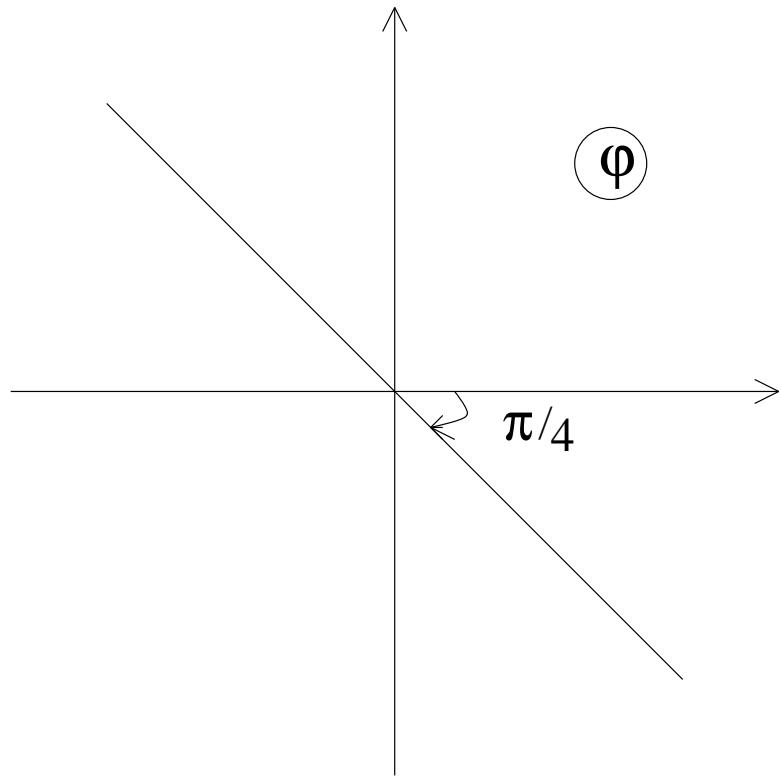


Fig.1 Transformation of the integration contour in the complex  $\Phi$  plane